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## (54) Colorimeter

(57) A probe colorimeter has at least one light-gathering rod probe 13 held captive in a non-transparent block 12 with the lower end extending below said block and the upper end extending into a chamber 20 in the block. The block is mounted for sliding vertical movement on two spaced apart pillars 11 upstanding from the upper surface of a light box 10, and means being provided to move the block up or down on the pillars. The light box has a light source 23 positioned between the roots of the pillars. A photosensor 21 is mounted

in chamber 20, in vertical optical alignment with the source. A tray or plate 33 having a solution-containing well 34 with a transparent base is positioned above the light box with the well base in registry above the light source and the block is lowered for the probe to dip into the solution. The embodiment of Fig. 4 has a plurality of probes 13 and the corresponding apparatus for measurements on a plurality of solutions 21 is preferably a photoresistor and the change of current due to absorption is detected by a balance circuit to feed a multiway switch or multiplexer.

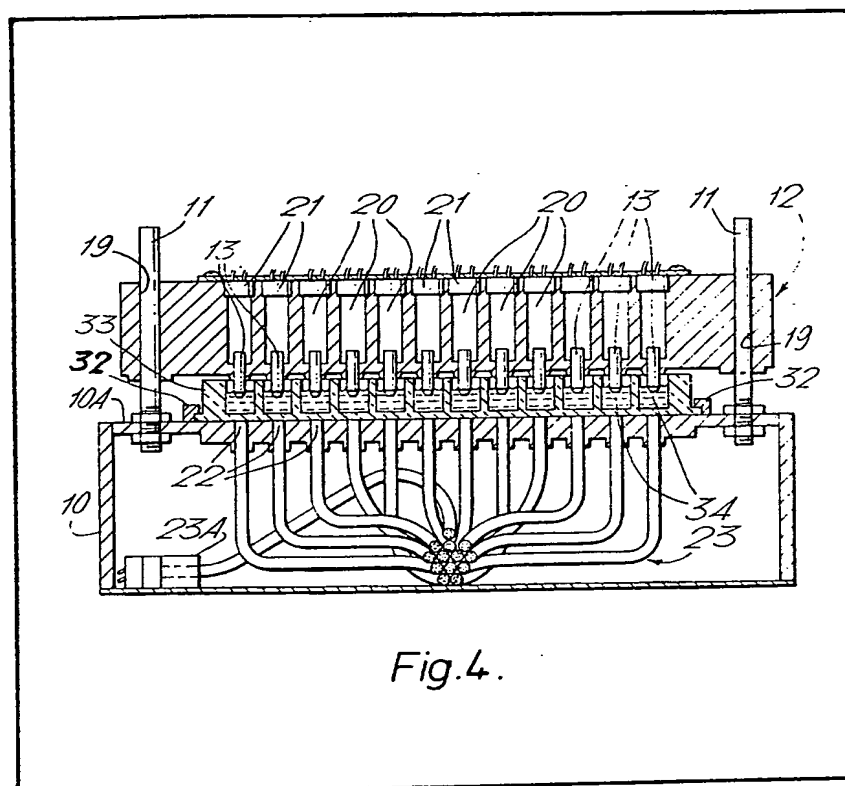


Fig.4.

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Fig.1.

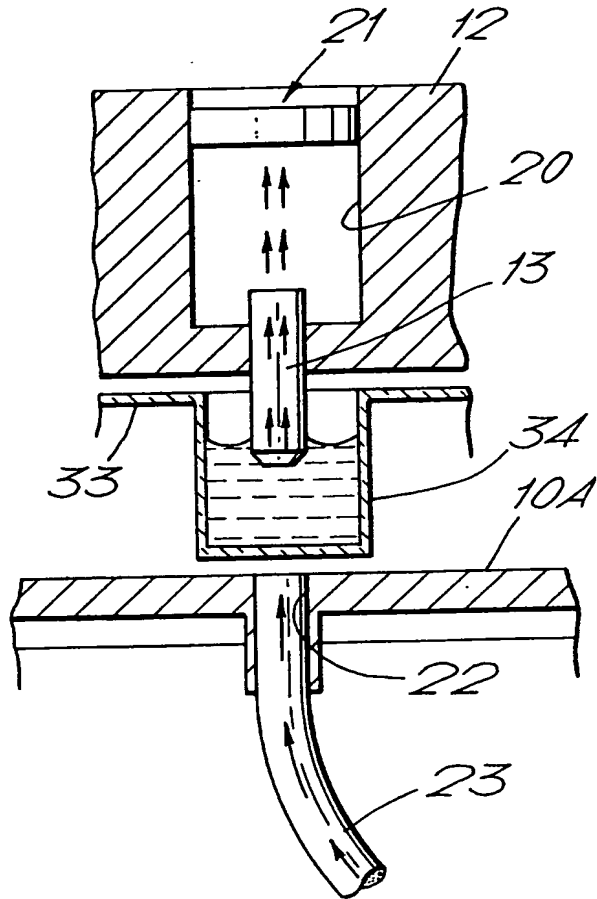
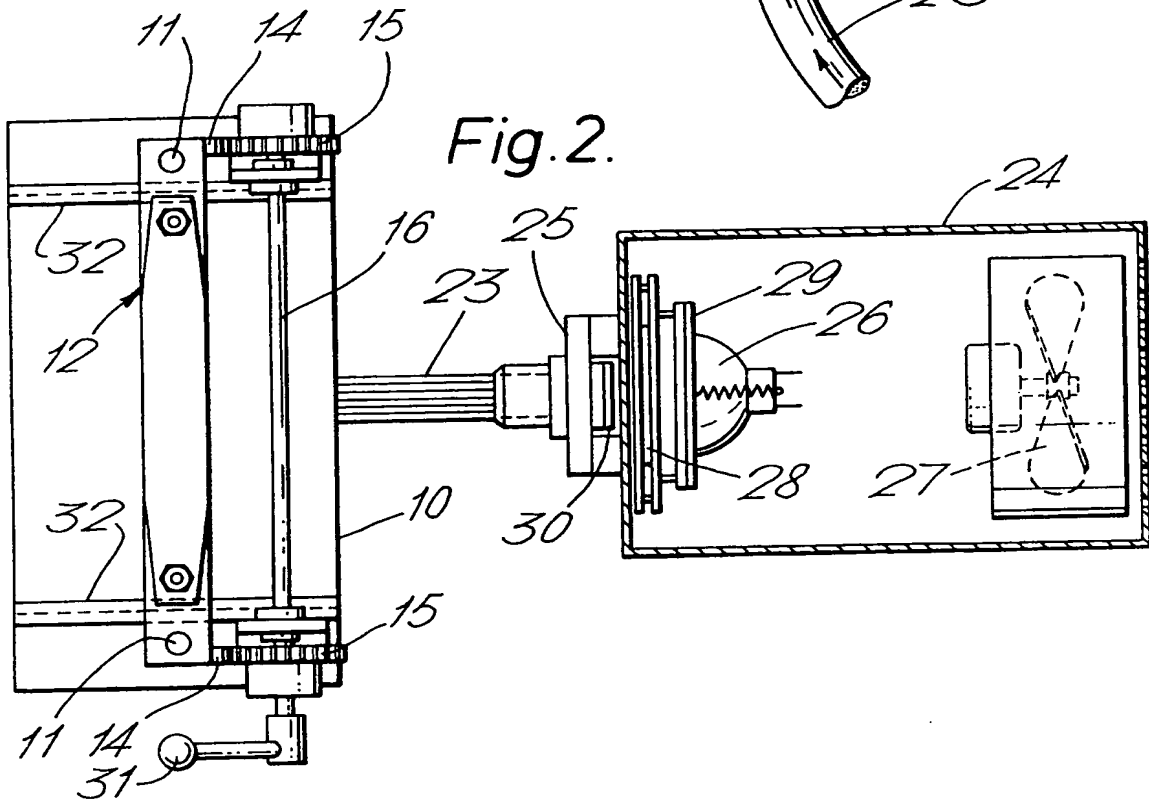


Fig.2.



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Fig.3.

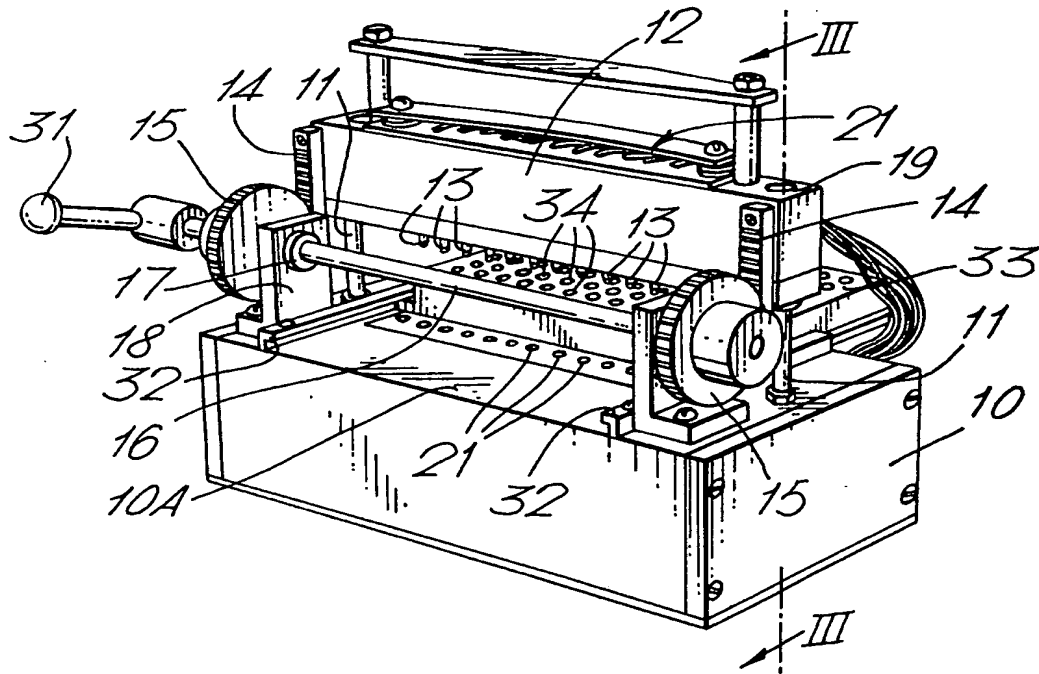
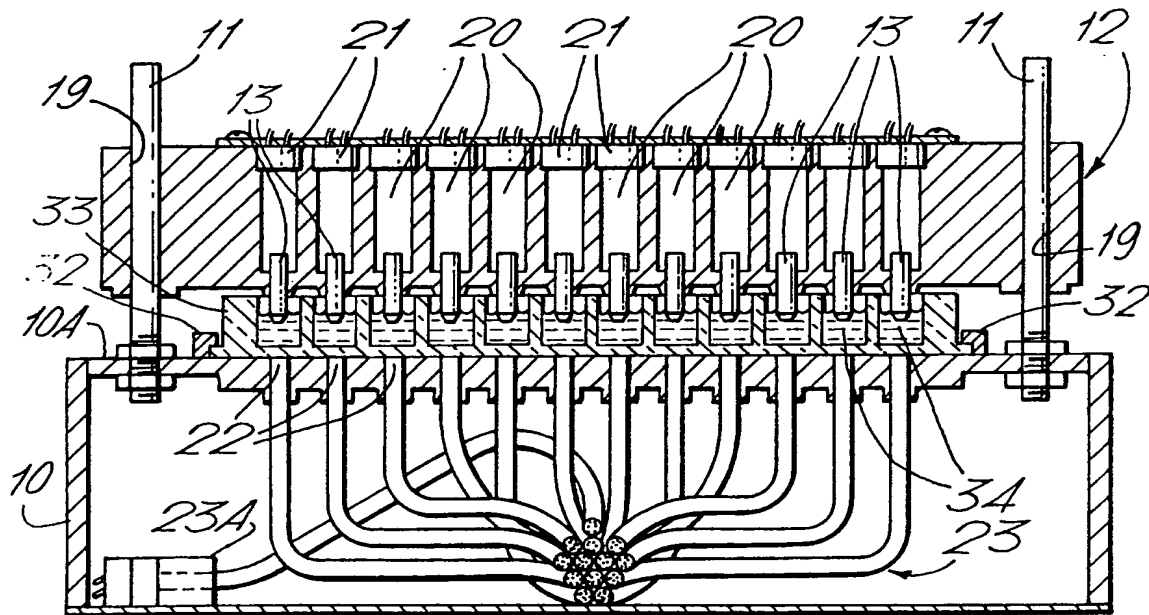


Fig.4.



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Fig.5.

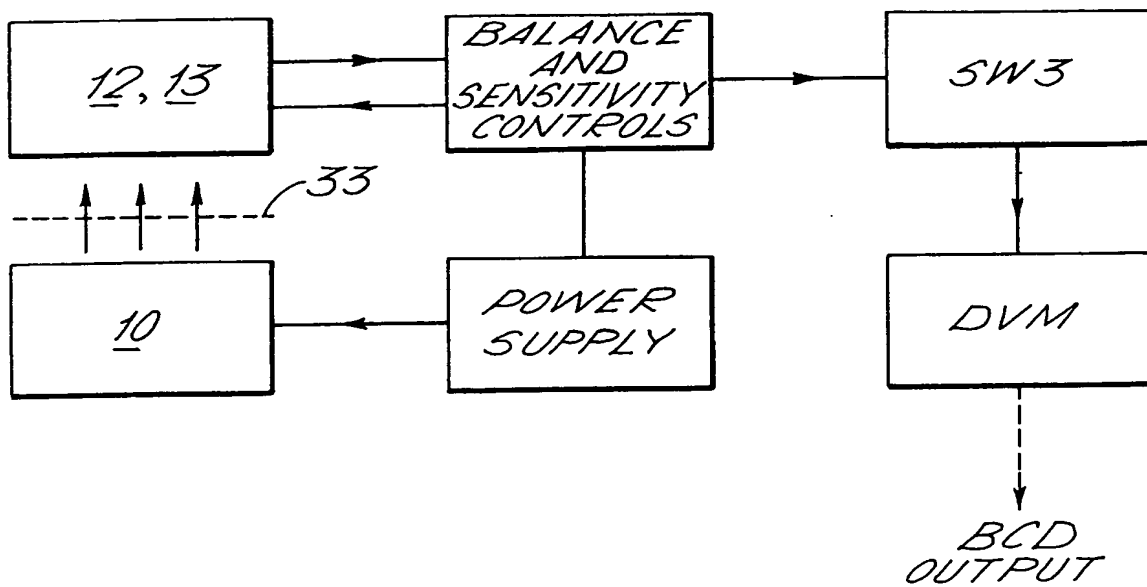
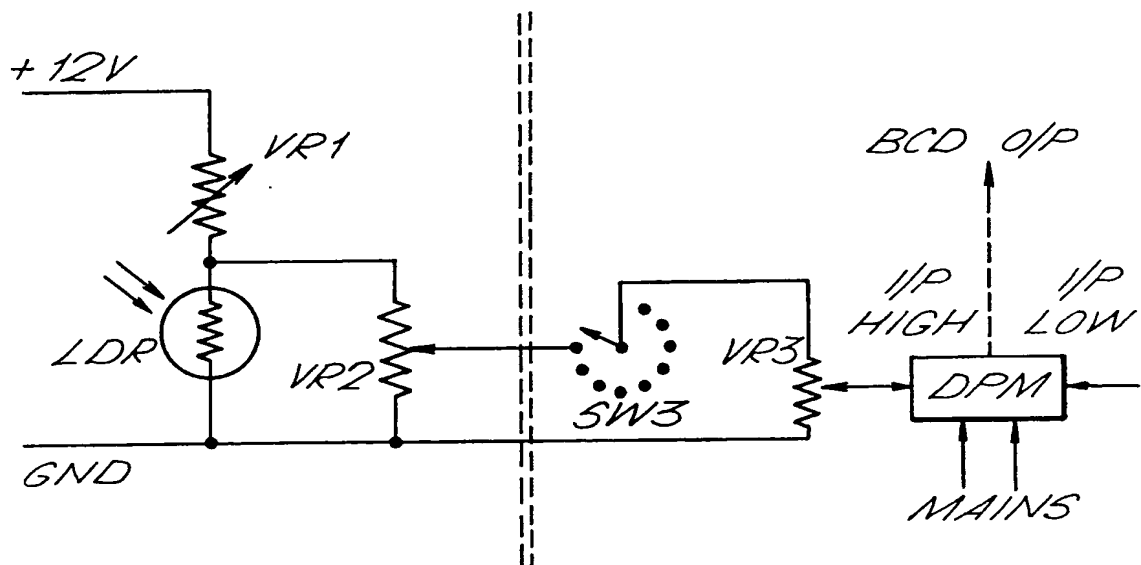


Fig.6.



## SPECIFICATION Colorimeters

This invention relates to a probe colorimeter in which a light source, a light-gathering probe and a photo-sensitive device are in vertical optical alignment with the probe being spaced above the light source, means for supporting a tray or plate having an array of solution-containing wells being provided between the light source and the probe, the probe extending down into a well with its lower face immediately above the meniscus of the solution.

Heretofore, this type of colorimeter has suffered from the disadvantages in that it has only been possible to determine the colour intensity of a solution in one well at a time, and from problems caused by the shape of the meniscus of the solution, and the "lens" effect thereof.

It is an object of the present invention to obviate or mitigate these above-described disadvantages.

According to a first aspect of the present invention, a colorimeter comprises a light-gathering rod probe arranged for vertical movement towards or away from a light source with which it is in optical alignment and between which a solution-containing well can be positioned, the light source being provided by a light emitting device housed in a box below said probe, the light being emitted through an aperture in the top of said box, the probe being captive in a non-transparent block with the lower end of the probe extending therebelow and with the upper end of the probe extending into a chamber in said block and being spaced from and in optical alignment with a photo-electric light sensitive device or detector in said chamber, the lower extent of travel of the lower end of said probe being determined to enable the lower face of the probe to be dipped into the solution in the well which has a transparent base when located in registry with and above the pertaining light source.

According to a second aspect of the present invention, a colorimeter comprises a row of light-gathering rod probes arranged for vertical movement towards or away from a row of similar numbered light sources with which they are in optical alignment and between which a row of similarly numbered solution-containing wells can be positioned, the light sources being provided by light emitting devices housed in a box below said probes, the light being emitted through apertures in the top of said box, the probes being similarly captive in a non-transparent block with the lower end of the probes extending therebelow and with the upper end of each probe extending into a chamber in said block and being spaced from and in optical alignment with a photoelectric light sensitive device or detector in said chamber, the lower extent of travel of the lower end of said probes being determined to enable the lower face of the probes to be dipped into the solutions in the row of wells which have transparent bases

when located in registry with and above the pertaining light sources.

According to a third aspect of the present invention, a colorimeter comprises a plurality of light-gathering rod probes arranged for vertical movement towards or away from a similar number of light sources, with which they are in optical alignment and between which a similar number of solution-containing wells can be positioned in registry the light sources being provided by light emitting devices housed in a box below said probes, the light being emitted through apertures in the top of said box, the probes being similarly captive in a non-transparent block with the lower ends of the probes extending therebelow and with the upper end of each probe extending into a chamber in said block and being spaced from and in optical alignment with a photo-electric light sensitive device or detector in said chamber, the lower extent of travel of the lower end of said probes being determined to enable the lower face of the probes to be dipped into the solutions in the row of wells which have transparent bases when located in registry with and above the pertaining light sources.

Preferably, the exposed surfaces of the or each probe external of the block, apart from the lower face of the or each probe, are covered with an optically opaque material.

Preferably also, the lower face of each probe is similarly shaped to eliminate the possibility of air bubbles being trapped thereunder when the lower faces of the probes are in solution.

An embodiment of the present invention will now be described, by way of example, with reference to the accompanying drawings, in which:—

Fig. 1 is a diagrammatic cross-sectional view of a detail of a colorimeter according to the present invention, and showing one probe dipped into a solution in a pertaining well;

Fig. 2 is a plan view of the colorimeter;

Fig. 3 is a perspective view of the colorimeter;

Fig. 4 is a cross-section along the line III—III of

Fig. 3;

Fig. 5 is a block diagram of the electronic system used; and

Fig. 6 is a balanced circuit for each photo-electric sensitive device.

A colorimeter comprises a rectangular box 10 from the upper surface 10A of which upstand two pillars 11 longitudinally spaced apart along the longitudinal midway line of said upper surface. A non-transparent block 12 of, for example aluminium, rectangular in both vertical and horizontal cross-sections is mounted on said pillars 11 for vertical movement relative thereto, a pillar 11 extending through a tubular passage 19 adjacent to each end of said block 12. A row of twelve light-gathering rod probes 13 are mounted in said block 12 with the upper ends of the probes held captive in the block 12 with the lower ends of the probes 13 extending downwardly from the lower face of the block 12. The probes 13 and

pillars 11 are in alignment. The exposed surfaces of the probes 13 below the block 12 with the exception of the lower faces thereof are covered in an optical opaque material to prevent stray light being picked up which may interfere with the sensitivity of the colorimeter. The block 12 is movable through two rack and pinion arrangements positioned on the same longitudinal side of the block, one rack 14 being located upright at each opposite end of said longitudinal side and parallel to the pertaining pillar, and a pinion 15 being carried at opposite ends of a shaft 16 parallel to the longitudinal axis of the block 12 with the teeth of the pinions 15 meshing with the teeth of the pertaining racks 14. The shaft 16 is journaled in two bearings 17, each carried in a bracket 18 adjacent to a pinion 15, the brackets 18 upstanding from the upper surface of the box 100. The shaft 16 is capable of manual restricted rotational movement, the determining factor for the restriction being the lower extent of movement required for the probes 13 as will be hereinafter described. A handle 31 is provided for the manual rotational movement of the shaft 16. The upper ends of the probes 13 each extend into an open-topped cylindrical chamber 20 drilled into the block 12 through the bottom thereof and the top of each chamber 20 is closed by a photo-electric sensitive device 21 or detector, such as a light dependent resistor, a Photodiode or Photomultiplier. The internal surfaces of each chamber 20 is covered with a dull black paint to prevent light reflections. The longitudinal axis of a probe 13 lies along the same line as the axis of the pertaining chamber 20.

The box 10 has a row of twelve similar apertures 22 in the upper surface 10A thereof and extending between the roots of the two pillars 11 each having a light emitting device 23 therebelow and housed in the box 10 to emit light therethrough. The light-emitting device 23 and the pertaining probe 13 and photo-electric sensitive device 21 are in optical alignment whereby light of a suitable wavelength or wavelength characteristic is passed onto the lower face of pertaining probe 13 and thence onto the device 21. Light with the desired properties may be directed through the light-emitting devices formed by fibre optic light guides supplied with light from a light-intensity quartz/iodine projector lamp 26 housed in a separate casing 24 external of the box 10. A holder 25 is provided externally of the casing 24 for mounting the fibre optic light guides in front of the lamp 26 and for positioning of interference filters as shown at 30 between the lamp 26 and the guides. The casing 24 also houses an electric fan 27 for cooling the air in the casing 24 while the lamp 26 is switched on, and a heat filter 28 is mounted internally of the casing 24 and in front of the lamp 26 which is secured in a mounting 29. Alternatively, each light emitting device is an electric light bulb, the light from which may be either filtered or unfiltered, or diffused or non-diffused depending on the particular application.

Means for supporting a tray or plate 33 having an array of solution-containing wells having at least transparent bases is provided by two guides 32 provided above the upper surface 10A of the box 10, the guides 32 transversing the upper surface of the box 10 at right angles to the block 12. The tray 33 has a series of rows of twelve wells 34 each extending across its length to enable twelve different solutions whose colour intensity is to be determined to be in registry over the twelve apertures 22 and on manually moving the handle 31, causing the lower faces of the probes 12 to dip into the solutions in the pertaining wells 34. The lower extent of movement of the lower faces of the probes is determined to have a constant distance between them and the bottom of the pertaining wells so as to maintain a constant optical path length in the solutions. It has been found in test that with a flat lower face on a probe, bubbles may accumulate thereunder when it is in solution. These bubbles can be removed by shaping the lower face to eliminate this, for example by having the lower face shaped as an inverted truncated cone, the conical surface of the lower face also being covered with an optical opaque material, such as dull black paint. The remaining bottom circular face is polished to minimise reflective losses at the face. Other ways of removing the entrapped bubbles may be

- (1) vibrating the solution in such a fashion as to remove the bubbles;
- (2) adding to the solution or coating the lower face of the probes with a substance to reduce adhesion of the bubbles; or
- (3) applying a vacuum.

The colorimeter above-described has been developed to obtain quantitative optical transmission data in order that the concentration of substances or solutions having the correct optical properties may be determined. The substances may be either dissolved in solution or suspended in a suitable medium. The solution is orientated in the optical beam of light in such a way that the light transmission is attenuated either by absorption or scattering. The measurements from the photo-electric sensitive devices may be made on the solutions in the wells 34 of the tray 33 either simultaneously or sequentially.

The electronics of each photo-electric sensitive device are such that a change in electronic output is generated in response to a change in light level at the lower face of the probe dipping below the surface of the solution.

Electrical stability of the colorimeter can be further ensured by incorporating sensors to detect changed light levels at the light source or by means of a "blank" well so that compensation may be taken care of electronically, and a spare fibre-optic light guide 23A may be provided for this purpose.

Preferably, cadmium sulphide light dependent resistors are used for the photo-electric sensitive devices because they have a peak spectral

response in the visible region, and the probes are of polymethylmethacrylate. The tray or plate may be polystyrene microtiter or microculture plate having flat-bottomed wells.

5 The circuitry used in this embodiment comprises a block diagram shown in Fig. 5, and twelve balanced circuits, one for each photo-electric sensitive device of which one is shown in Fig. 6. The change in current through the sensitive  
10 device is detected by the balance circuit and transferred as a voltage measurement to a 12-way switch SW3 or multiplexer.

The mode of operation may be selected by a change-over switch, which permits the electrical  
15 output from the sensitive devices to be transferred either manually *via* 12-way switch SW3, or automatically *via* the multiplexer, to a digital voltage meter (DVM).

A potentiometer VR3 (Figure 6) acts as a  
20 voltage divider, bringing the voltage output of the balance circuit within the range of the DVM. A 200 mV DVM with Binary Coded Decimal (BCD) output was used so that the readings could be transferred *via* suitable interfaces to recordings or  
25 computing equipment.

Two stabilized power supplies are used. The first provides power for the balance circuits; the second (a regulator with associated circuitry) provides the high current necessary for the high  
30 intensity lamp 26 and also provides an isolated circuit for the multiplexer. All the electronics except the photo-electric sensitive devices are housed in a metal box, the front panel of which is used to mount the potentiometers, meter, and  
35 switches.

An analogue multiplexer enables the output from the twelve sensitive devices to be scanned sequentially. The scanning process is initiated by a push switch, which is mounted on the front  
40 panel of the box containing the electronics. The rate of scanning can be internally adjusted by altering the potentiometers, the maximum speed being dependent on the settling time of the DVM. The above-described colorimeter scans the twelve  
45 wells in a single row in approximately 6 secs giving an overall plate reading rate of 1.5 mins.

The colorimeter, prior to use, was calibrated by using a microtiter plate containing 200  $\mu$ l of water in one row of wells and 200  $\mu$ l of a  
50 standard solution ( $A=1.0$ ) in another. The wells containing water were positioned under the probes and the probes lowered into the water. The reading from an individual well was selected by the 12-way switch and its associated  
55 potentiometer (VR1) was adjusted to give a zero of a slightly +ve reading on the DVM. This was repeated for each of the 12 wells in the row. The plate was moved, after elevation of the block to read the wells containing the standard solution.  
60 The sensitivity setting potentiometers (VR2) were adjusted to give the required uniform reading on the meter for each of the 12 wells. This sequence of calibrating the blank and standard solutions was repeated as necessary until readings were  
65 stable to compensate for the slight interaction

between the zero and sensitivity-setting potentiometers (VR1 and VR2).

In a modification of the above-described embodiment of the colorimeter, only one probe,  
70 one light source and one photo-electric light sensing device are provided, all in optical alignment. This is for particular use in connection with determining quantitative optical transmission data of a substance in solution in a  
75 single well or container.

In a further embodiment of the above-described embodiment of the colorimeter, a plurality of optically aligned probes, light sources and photo-electric light sensitive devices are  
80 provided, the plurality being arranged as desired in regular or irregular formation, or in rows of regular or irregular numbers, the wells in the tray or plate of wells being similarly arranged.

### Claims

85 1. Colorimeter comprises a light-gathering rod probe arranged for vertical movement towards or away from a light source with which is in optical alignment and between which a solution-containing well can be positioned, the light source  
90 being provided by a light emitting device housed in a box below said probe, the light being emitted through an aperture in the top of said box, the probe being captive in a non-transparent block with the lower end of the probe extending  
95 therebelow and with the upper end of the probe extending into a chamber in said block and being spaced from and in optical alignment with a photo-electric light sensitive device or detector in said chamber, the lower extent of travel of the  
100 lower end of said probe being determined to enable the lower face of the probe to be dipped into the solution in the well which has a transparent base when located in registry with and above the pertaining light source.

105 2. A colorimeter comprises a row of light-gathering rod probes arranged for vertical movement towards or away from a row of similar numbered light sources with which they are in optical alignment and between which a row of  
110 similarly numbered solution-containing wells can be positioned, the light sources being provided by light emitting devices housed in a box below said probes, the light being emitted through apertures in the top of said box, the probes being similarly  
115 captive in a non-transparent block with the lower ends of the probes extending therebelow and with the upper end of each probe extending into a chamber in said block and being spaced from and in optical alignment with a photo-electric light-sensitive device or detector in said chamber, the  
120 lower extent of travel of the lower end of said probes being determined to enable the lower face of the probes to be dipped into the solutions in the row of wells which have transparent bases when located in registry with and above the  
125 pertaining light sources.

3. Colorimeter comprises a plurality of light-gathering rod probes arranged for vertical movement towards or away from a similar

number of light sources with which they are in optical alignment and between which a similar number of solution-containing wells can be positioned in registry the light sources being  
5 provided by light emitting devices housed in a box below said probes, the light being emitted through apertures in the top of said box, the probes being similarly captive in a non-transparent block with the lower ends of the  
10 probes extending therebelow and with the upper end of each probe extending into a chamber in said block and being spaced from and in optical alignment with a photo-electric light sensitive device or detector in said chamber, the lower  
15 extent of travel of the lower end of said probes being determined to enable the lower face of the probes to be dipped into the solutions in the row of wells which have transparent bases when

located in registry with and above the pertaining  
20 light sources.

4. A colorimeter as claimed in claim 1, 2 or 3 wherein the exposed surface of the or each probe external of the block, apart from the lower face of the or each probe are covered with an optically  
25 opaque material.

5. A colorimeter as claimed in claim 1, 2, 3 or 4, wherein the lower face of each probe is similarly shaped to eliminate the possibility of air bubbles being trapped thereunder when the lower  
30 faces of the probes are in solution.

6. A colorimeter substantially as hereinbefore described with reference to Fig. 1 of the accompanying drawings.

7. A colorimeter substantially as hereinbefore  
35 devised with reference to Figs. 2, 3, 4, 5 and 6 of the accompanying drawings.

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